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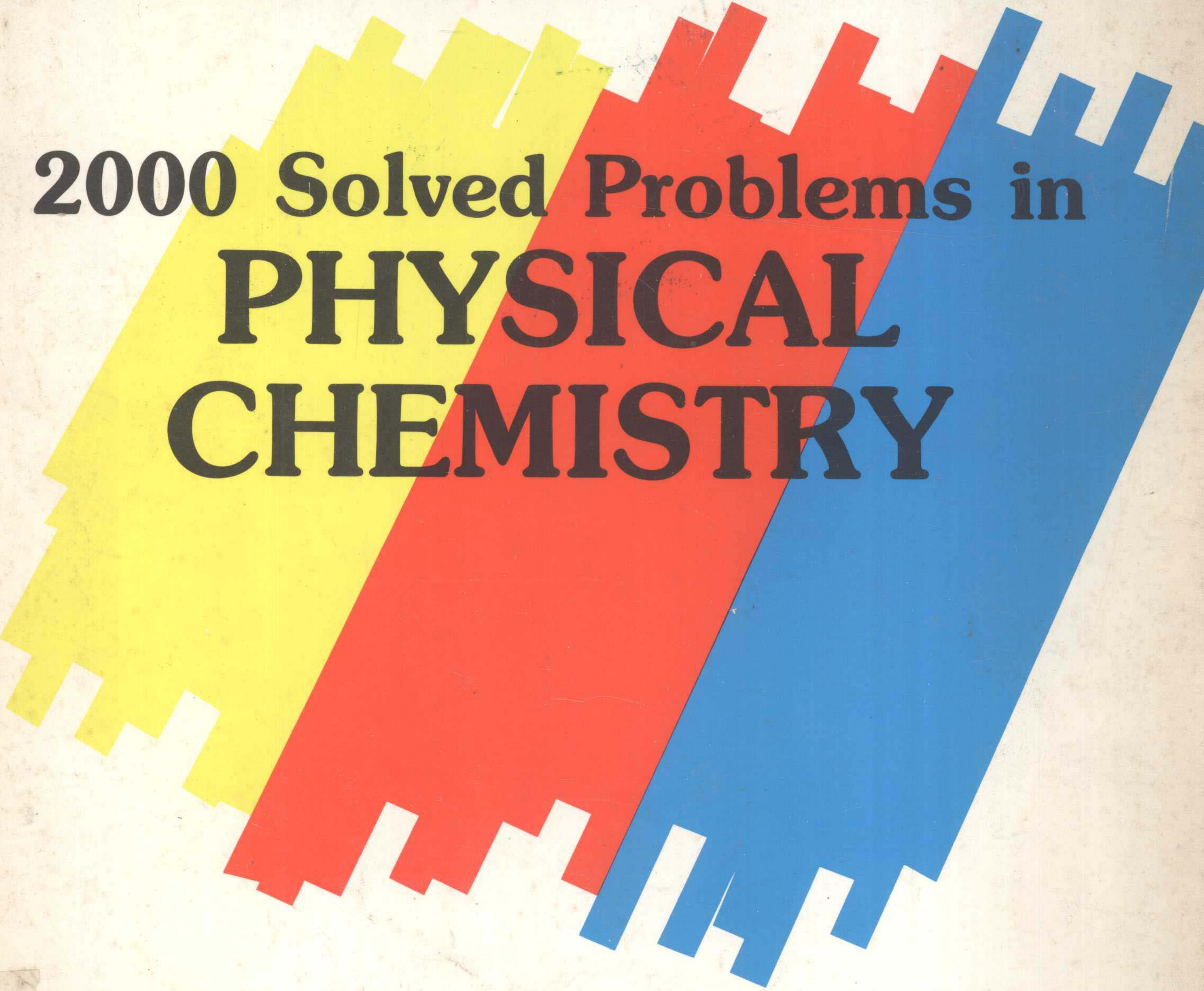

2000 Solved Problems in
PHYSICAL CHEMISTRY

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2000 SOLVED PROBLEMS IN

PHYSICAL CHEMISTRY

by

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College of Charleston

McGRAW-HILL PUBLISHING COMPANY
New York St. Louis San Francisco Auckland Bogotá Caracas
Hamburg Lisbon London Madrid Mexico Milan Montreal
New Delhi Oklahoma City Paris San Juan São Paulo
Singapore Sydney Tokyo Toronto

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Project supervision was done by The Total Book.

Library of Congress Cataloging-in-Publication Data

Metz, Clyde R.
2000 solved problems in physical chemistry / by Clyde Metz.
p. cm.—(Schaum's solved problems series)
ISBN 0-07-041717-2(HC)
ISBN 0-07-041716-4(PBK)
1. Chemistry, Physical and theoretical—Problems, exercises, etc. I. Title.
II. Title: Two thousand solved problems in physical chemistry. III. Series.
QD456.M39 1990
541.3′076—dc20 89-2616
CIP

2 3 4 5 6 7 8 9 0 SHP/SHP 8 9 4 3 2 1 0 9

ISBN 0-07-041717-2{HC}
ISBN 0-07-041716-4{PBK}

To the Student

OK, so now you have your first homework assignment due in physical chemistry. Where do you begin? How do you solve the problems? What should the answers that you submit look like? These questions, as well as several others, are likely to be on your mind. The purpose of this book is to help you to prepare your assignments and to review for examinations.

The first step in doing a homework assignment is to understand the material before trying to solve any problems. Reading the chapter in your text several times, looking at any example problems in the text, and rewriting your lecture notes will help in understanding the material. Now you are ready to take the second step, to solve the problems.

Unless a problem is particularly difficult, usually the data can be used with an equation or two to give the desired answer. The general format used in this book—identification of the proper equation or relationship, substitution of the data (with proper units), and the calculation of the desired answer (to the proper number of significant figures)—is the format that you should use in solving your problems. Although the method for solving a problem should be recognizable within a few minutes, the actual solving may take longer.

This book will not serve as an answer book to your text, because all the problems are original. However, it will serve as a "how to" manual, because the problems are similar in content and style to those found in your physical chemistry textbook. The organization of this book is exactly parallel to that found in *Schaum's Outline of Theory and Problems of Physical Chemistry*, 2d ed., McGraw-Hill (1989), and the two books make a complete set of supplementary materials for examination reviews and for learning to solve problems in physical chemistry.

I would like to acknowledge the tremendous contribution made by my wife, Jennie, in the preparation of the manuscript from my handwritten scrawlings.

CONTENTS

CHAPTER 1

Gases and the Kinetic-Molecular Theory

1.1 TEMPERATURE AND PRESSURE

1.1 The normal boiling points of liquid nitrogen, oxygen, and helium are −195.8 °C, −297.332 °F, and 4.25 K, respectively. Which element has the lowest boiling point? Which element will remain a liquid after samples of the other two elements have evaporated?

▮ The temperature (T) in kelvins at which N_2 boils is

$$T/(\mathrm{K}) = T/(^\circ\mathrm{C}) + 273.15 = -195.8 + 273.15 = 77.4 \tag{1.1}$$

The boiling point of O_2 in units of Celsius degrees is

$$T/(^\circ\mathrm{C}) = \tfrac{5}{9}[T/(^\circ\mathrm{F}) - 32] = \tfrac{5}{9}(-297.332 - 32) = -182.962 \tag{1.2}$$

which upon substitution into *(1.1)* gives

$$T/(\mathrm{K}) = -182.962 + 273.15 = 90.188$$

Helium has the lowest point at 4.25 K. Nitrogen will boil at 77.4 K, leaving the oxygen sample in the liquid state. The oxygen will not boil until it reaches a temperature of 90.188 K.

1.2 At what temperature will both the Celsius and Fahrenheit scales read the same value?

▮ Substituting $T/(^\circ\mathrm{C}) = T/(^\circ\mathrm{F}) = T$ into *(1.2)* and solving gives

$$T = \tfrac{5}{9}(T - 32) = -40$$

Both temperature scales are equivalent at $-40\ ^\circ\mathrm{C} = -40\ ^\circ\mathrm{F}$.

1.3 Combine *(1.1)* and *(1.2)* to define the Rankine temperature scale (°R), the absolute Fahrenheit temperature scale.

▮ The general form of the defining equation is

$$T/(^\circ\mathrm{R}) = T/(^\circ\mathrm{F}) + k$$

Solving *(1.2)* for $T/(^\circ\mathrm{F})$ in terms of $T/(^\circ\mathrm{C})$ and substituting gives

$$T/(^\circ\mathrm{R}) = \tfrac{9}{5}[T/(^\circ\mathrm{C})] + 32 + k$$

Solving *(1.1)* for $T/(^\circ\mathrm{C})$ in terms of $T/(\mathrm{K})$ and substituting gives

$$T/(^\circ\mathrm{R}) = \tfrac{9}{5}[T/(\mathrm{K}) - 273.15] + 32 + k$$

Recognizing that $T/(^\circ\mathrm{R}) = T/(\mathrm{K}) = 0$ at absolute zero,

$$0 = \tfrac{9}{5}(0 - 273.15) + 32 + k$$

$$k = 459.67$$

Thus the Rankine temperature scale is defined as

$$T/(^\circ\mathrm{R}) = T/(^\circ\mathrm{F}) + 459.67$$

1.4 The vapor pressure of water is 4.58 torr at 0 °C and 760.00 torr at 100 °C. Assume that a water temperature scale (°W) is based on this thermodynamic property with $0\ ^\circ\mathrm{C} = 0\ ^\circ\mathrm{W}$ and $100\ ^\circ\mathrm{C} = 100\ ^\circ\mathrm{W}$. Find the relation between this hypothetical scale and the Celsius scale. Express 50 °C in units of °W. The vapor pressure of water at 50 °C is 92.51 torr.

▮ If y_2 and y_1 represent the values of a thermodynamic property at fixed temperatures T_2 and T_1, respectively, then the temperature T that corresponds to the value y for the thermodynamic property is defined as

$$T = T_1 + \frac{y - y_1}{y_2 - y_1}(T_2 - T_1) \tag{1.3}$$

In this case, the fixed temperatures are 0 °W and 100 °W, giving

$$T = 0\ {}^\circ\mathrm{W} + \frac{P - 4.58\ \mathrm{torr}}{760.00\ \mathrm{torr} - 4.58\ \mathrm{torr}}(100\ {}^\circ\mathrm{W} - 0\ {}^\circ\mathrm{W})$$

which can be written as

$$T/({}^\circ\mathrm{W}) = (0.132\,38)[P/(\mathrm{torr}) - 4.58]$$

On this scale, 50 °C is equivalent to

$$T/({}^\circ\mathrm{W}) = (0.132\,38)(92.51 - 4.58) = 11.64$$

Note that this hypothetical temperature scale is nonlinear.

1.5 The temperature dependence of the length (l) of a platinum rod is given by

$$l = l_0\{1 + \alpha[T/({}^\circ\mathrm{C})] + \beta[T/({}^\circ\mathrm{C})]^2\}$$

where $\alpha = 8.68 \times 10^{-6}$, $\beta = 1.3 \times 10^{-9}$, and l_0 is the length at 0 °C. A nonlinear temperature scale (°Pt) is defined in terms of this thermodynamic property such that 0 °Pt = 0 °C and 100 °Pt = 100 °C. Find the relation between this hypothetical scale and the Celsius scale. Express 50 °C and 500 °C in units of °Pt.

■ The fixed points in *(1.3)* are 0 °Pt, where $y(0\ {}^\circ\mathrm{Pt}) = l_0$, and 100 °Pt, where $y(100\ {}^\circ\mathrm{Pt}) = l(100\ {}^\circ\mathrm{C})$ and $y = l$. Thus,

$$T = 0\ {}^\circ\mathrm{Pt} + \frac{l - l_0}{l(100\ {}^\circ\mathrm{C}) - l_0}(100\ {}^\circ\mathrm{Pt} - 0\ {}^\circ\mathrm{Pt})$$

$$T/({}^\circ\mathrm{Pt}) = \frac{l_0\{1 + \alpha[T/({}^\circ\mathrm{C})] + \beta[T/({}^\circ\mathrm{C})]^2\} - l_0}{l_0[1 + \alpha(100) + \beta(100)^2] - l_0}(100) = \frac{\alpha[T/({}^\circ\mathrm{C})] + \beta[T/({}^\circ\mathrm{C})]^2}{\alpha + 100\beta}$$

Expressing 50 °C and 500 °C on this temperature scale shows that the scale is nonlinear:

$$T/({}^\circ\mathrm{Pt}) = \frac{(8.68 \times 10^{-6})(50) + (1.3 \times 10^{-9})(50)^2}{8.68 \times 10^{-6} + (100)(1.3 \times 10^{-9})} = 49.6$$

$$T/({}^\circ\mathrm{Pt}) = \frac{(8.68 \times 10^{-6})(500) + (1.3 \times 10^{-9})(500)^2}{8.81 \times 10^{-6}} = 534$$

1.6 A hypothetical absolute temperature scale (°A) is defined by assigning 0 °C = 100 °A. What will be the normal boiling point of water on this scale?

■ The values of the thermodynamic property in *(1.3)* can be represented by $y_1 = y(0\ {}^\circ\mathrm{A}) = y(0\ \mathrm{K})$ and $y_2 = y(100\ {}^\circ\mathrm{A}) = y(0\ {}^\circ\mathrm{C}) = y(273.15\ \mathrm{K})$. For each temperature scale,

$$T = 0\ \mathrm{K} + \frac{y - y_1}{y_2 - y_1}(273.15\ \mathrm{K} - 0\ \mathrm{K})$$

$$T = 0\ {}^\circ\mathrm{A} + \frac{y - y_1}{y_2 - y_1}(100\ {}^\circ\mathrm{A} - 0\ {}^\circ\mathrm{A})$$

Solving the first equation for $(y - y_1)/(y_2 - y_1)$ and substituting into the second equation gives

$$T/({}^\circ\mathrm{A}) = \{[T/(\mathrm{K})]/(273.15)\}(100) = (0.366\,10)[T/(\mathrm{K})]$$

On this hypothetical scale, 100.00 °C = 373.15 K is

$$T/({}^\circ\mathrm{A}) = (0.366\,10)(373.15) = 136.61$$

1.7 Assume that a hypothetical temperature scale (°B) is based on the melting point (0 °B = 5.5 °C) and the normal boiling point (100 °B = 80.1 °C) of benzene. What is the freezing point of water on this scale?

■ The value of the thermodynamic property in *(1.3)* can be represented by $y_1 = y(5.5\ {}^\circ\mathrm{C}) = y(0\ {}^\circ\mathrm{B})$ and $y_2 = y(80.1\ {}^\circ\mathrm{C}) = y(100\ {}^\circ\mathrm{B})$. For each temperature scale,

$$T = 5.5\ {}^\circ\mathrm{C} + \frac{y - y_1}{y_2 - y_1}(80.1\ {}^\circ\mathrm{C} - 5.5\ {}^\circ\mathrm{C}) = 5.5\ {}^\circ\mathrm{C} + \frac{y - y_1}{y_2 - y_1}(74.6\ {}^\circ\mathrm{C})$$

$$T = 0\ {}^\circ\mathrm{B} + \frac{y - y_1}{y_2 - y_1}(100\ {}^\circ\mathrm{B} - 0\ {}^\circ\mathrm{B}) = \frac{y - y_1}{y_2 - y_1}(100\ {}^\circ\mathrm{B})$$

Solving the first equation for $(y - y_1)/(y_2 - y_1)$ and substituting into the second equation gives

$$T/(^\circ\mathrm{B}) = \frac{T/(^\circ\mathrm{C}) - 5.5}{74.6}(100)$$

On this hypothetical scale, 0 °C is

$$T/(^\circ\mathrm{B}) = \frac{0 - 5.5}{74.6}(100) = -7.4$$

1.8 Express each of the following values of pressure in units of pascals: **(*a*)** 32 psi, **(*b*)** 745 torr, **(*c*)** 14.6 mbar, **(*d*)** 12.7 atm, **(*e*)** 850 kPa, and **(*f*)** $8 \times 10^4\ \mathrm{N \cdot m^{-2}}$. Which pressure is the greatest?

▮ Using the conversion factors given in Table 1-1 gives

(*a*) $(32\ \mathrm{psi})[(6.89 \times 10^3\ \mathrm{Pa})/(1\ \mathrm{psi})] = 2.2 \times 10^5\ \mathrm{Pa}$
(*b*) $(745\ \mathrm{torr})[(1\ \mathrm{atm})/(760\ \mathrm{torr})][(101\,325\ \mathrm{Pa})/(1\ \mathrm{atm})] = 9.93 \times 10^4\ \mathrm{Pa}$
(*c*) $(14.6\ \mathrm{mbar})[(10^{-3}\ \mathrm{bar})/(1\ \mathrm{mbar})][(10^5\ \mathrm{Pa})/(1\ \mathrm{bar})] = 1.46 \times 10^3\ \mathrm{Pa}$
(*d*) $(12.7\ \mathrm{atm})[(101\,325\ \mathrm{Pa})/(1\ \mathrm{atm})] = 1.29 \times 10^6\ \mathrm{Pa}$
(*e*) $(850\ \mathrm{kPa})[(10^3\ \mathrm{Pa})/(1\ \mathrm{kPa})] = 8.5 \times 10^5\ \mathrm{Pa}$
(*f*) $(8 \times 10^4\ \mathrm{N \cdot m^{-2}})[(1\ \mathrm{Pa})/(1\ \mathrm{N \cdot m^{-2}})] = 8 \times 10^4\ \mathrm{Pa}$

The greatest pressure is 12.7 atm.

Table 1-1

$1\ \mathrm{Pa} = 1\ \mathrm{N \cdot m^{-2}} = 1\ \mathrm{kg \cdot m^{-1} \cdot s^{-2}}$
$1\ \mathrm{bar} = 10^5\ \mathrm{Pa}$
$1\ \mathrm{atm} = 101\,325\ \mathrm{Pa}$
$1\ \mathrm{atm} = 760\ \mathrm{torr}$
$1\ \mathrm{psi} = 6894.7572\ \mathrm{Pa}$

1.9 Calculate the pressure exerted by a 760-mm column of mercury.

▮ The pressure (P) is given by

$$P = f/A = mg/A = mgh/V = \rho gh \tag{1.4}$$

where f is force, A is area, m is mass, g is the gravitational acceleration, h is the height of the liquid column, V is the volume, and ρ is the density of the liquid. Substituting numerical values gives

$$\begin{aligned} P &= (13.5955\ \mathrm{g \cdot cm^{-3}})\frac{10^{-3}\ \mathrm{kg}}{1\ \mathrm{g}}\left(\frac{10^2\ \mathrm{cm}}{1\ \mathrm{m}}\right)^3(9.806\,65\ \mathrm{m \cdot s^{-2}})(760\ \mathrm{mm})\frac{10^{-3}\ \mathrm{m}}{1\ \mathrm{mm}}\left(\frac{1\ \mathrm{N}}{1\ \mathrm{kg \cdot m \cdot s^{-2}}}\right) \\ &= 101\,328\ \mathrm{N \cdot m^{-2}} = 101\,328\ \mathrm{Pa} \end{aligned}$$

1.10 Dibutyl phthalate is commonly used as a liquid in manometers. What pressure is equivalent to a centimeter of this liquid?

▮ The pressure is given by *(1.4)* as

$$\begin{aligned} P &= (1.0465\ \mathrm{g \cdot cm^{-3}})\frac{10^{-3}\ \mathrm{kg}}{1\ \mathrm{g}}\left(\frac{10^2\ \mathrm{cm}}{1\ \mathrm{m}}\right)^3(9.806\,65\ \mathrm{m \cdot s^{-2}})(1\ \mathrm{cm})\frac{10^{-2}\ \mathrm{m}}{1\ \mathrm{cm}}\left(\frac{1\ \mathrm{N}}{1\ \mathrm{kg \cdot m \cdot s^{-2}}}\right) \\ &= 102.63\ \mathrm{N \cdot m^{-2}} \end{aligned}$$

1.11 What is the approximate mass of the atmosphere of the earth? Assume the radius of the earth to be 6370 km.

▮ The surface area of the earth is given by

$$A = 4\pi r^2 = 4\pi(6370\ \mathrm{km})^2\left(\frac{10^3\ \mathrm{m}}{1\ \mathrm{km}}\right)^2 = 5.10 \times 10^{14}\ \mathrm{m^2}$$

The mass of air that produces a pressure of 101 325 Pa is given by *(1.4)* as

$$\begin{aligned} m &= \frac{PA}{g} \\ &= \frac{(101\,325\ \mathrm{Pa})[(1\ \mathrm{kg \cdot m^{-1} \cdot s^{-2}})/(1\ \mathrm{Pa})](5.10 \times 10^{14}\ \mathrm{m^2})}{9.81\ \mathrm{m \cdot s^{-2}}} = 5.27 \times 10^{18}\ \mathrm{kg} \end{aligned}$$

1.12 At what altitude will the atmospheric pressure decrease from 1.00 bar to 0.50 bar? Assume that the average molar mass of air is 29 $\text{g} \cdot \text{mol}^{-1}$.

▮ The atmospheric pressure at a height h above sea level is related to the atmospheric pressure at sea level (P_0) by the *barometric formula*

$$P = P_0\, e^{-gMh/RT} \tag{1.5}$$

where M is the molar mass and R is the gas constant. Solving *(1.5)* for h and substituting values gives

$$h = \frac{-RT \ln (P/P_0)}{gM}$$

$$= \frac{-(8.314\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})[(1\ \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2})/(1\ \text{J})](298\ \text{K}) \ln (0.50/1.00)}{(9.81\ \text{m} \cdot \text{s}^{-2})(29 \times 10^{-3}\ \text{kg} \cdot \text{mol}^{-1})} = 6.0 \times 10^3\ \text{m}$$

1.13 At sea level (Charleston, S.C.) the pressure of nitrogen in the atmosphere is 0.80 bar and the pressure of oxygen is 0.20 bar at 25 °C. What are the respective pressures at an altitude of 1600 m (Denver, Col.) at 25 °C? Which city has the greater oxygen-to-nitrogen ratio in the air?

▮ For each gas, *(1.5)* gives

$$P(\text{N}_2) = (0.80\ \text{bar}) \exp\left(-\frac{(9.81\ \text{m} \cdot \text{s}^{-2})(28 \times 10^{-3}\ \text{kg} \cdot \text{mol}^{-1})(1600\ \text{m})}{(8.314\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298\ \text{K})[(1\ \text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2})/(1\ \text{J})]}\right) = 0.67\ \text{bar}$$

$$P(\text{O}_2) = (0.20) \exp\left(-\frac{(9.81)(32 \times 10^{-3})(1600)}{(8.314)(298)}\right) = 0.16\ \text{bar}$$

At sea level,

$$P(\text{O}_2)/P(\text{N}_2) = (0.20\ \text{bar})/(0.80\ \text{bar}) = 0.25$$

and at 1600 m,

$$P(\text{O}_2)/P(\text{N}_2) = 0.16/0.67 = 0.24$$

The air in Charleston is slightly richer in oxygen than the Denver air.

1.14 Compare the atmospheric pressure values predicted by *(1.5)* for dry air with the following actual values:

***h*/(km)**	0	10	20	30	40	50	60	70	80	90	100
***P*/(Pa)**	101 325	27 998	5600	1267	320	100	28	7.2	1.3	0.25	0.056

Assume $M = 29.0 \times 10^{-3}\ \text{kg} \cdot \text{mol}^{-1}$ and $T = 237\ \text{K}$.

▮ A plot of $\ln [P/(\text{Pa})]$ against $h/(\text{km})$ is shown in Fig. 1-1. The symbols represent the actual values of pressure, and the line represents the values calculated using *(1.5)*. The agreement is excellent, especially considering the fact that the values of T range from 190 K to 290 K.

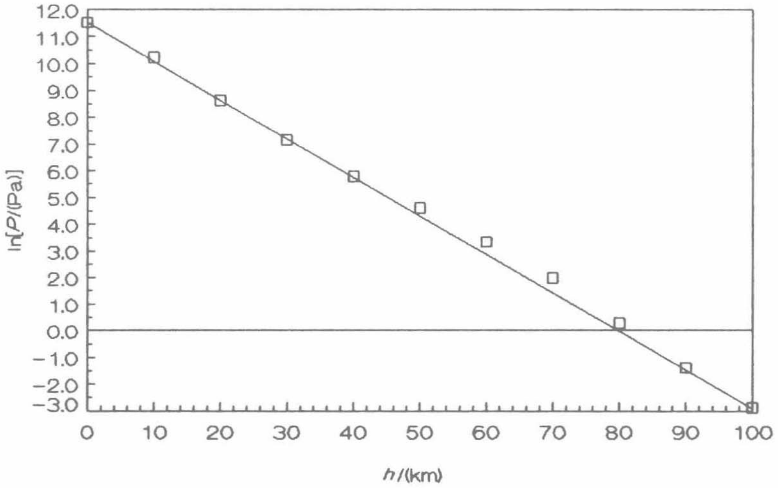

Fig. 1-1

1.15 How is the pressure predicted by *(1.5)* affected by the small decreases in g and in T that occur as the altitude increases?

▮ As T decreases with increasing h, the exponential term in *(1.5)* becomes slightly smaller, and so P decreases somewhat faster than if T were constant. As g decreases with increasing h, the exponential term in *(1.5)* becomes slightly larger, and so P decreases somewhat slower than if g were constant. (The two decreases offset each other to a certain extent.)

1.2 LAWS FOR IDEAL GASES

1.16 Identify which of the following plots for a fixed amount of an ideal gas at constant temperature will be linear: **(*a*)** P against V, **(*b*)** P against $(1/V)$, **(*c*)** PV against P, and **(*d*)** $(1/P)$ against V. Determine the slope of the straight line in each linear plot.

▮ The pressure-volume behavior for a fixed amount of an ideal gas under isothermal conditions is given by *Boyle's law* as

$$PV = k \tag{1.6}$$

where k is a constant. The linear forms of *(1.6)* are **(*b*)** $P = k(1/V)$ with the slope equal to k, **(*c*)** $PV = k$ with the slope equal to 0, and **(*d*)** $1/P = (1/k)V$ with the slope equal to $1/k$.

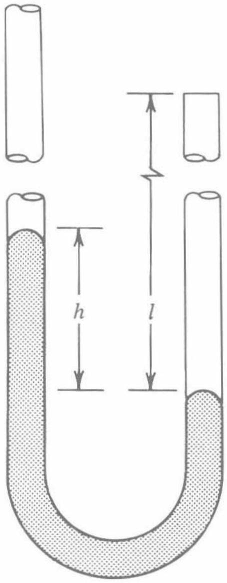

Fig. 1-2

1.17 The apparatus used by Boyle is shown schematically in Fig. 1-2. The length of the trapped air in the right arm is given by l (measured in arbitrary units), and the pressure difference in the arms is determined from h, the difference in the heights of the mercury columns in the arms. If the atmospheric pressure on the left arm is $29\frac{2}{16}$ inches of mercury, show that the following data agree with *(1.6)*:

l	44	38	32	26	20
h/(inches Hg)	$2\frac{13}{16}$	$7\frac{14}{16}$	$15\frac{1}{16}$	$25\frac{3}{16}$	$41\frac{9}{16}$

▮ The pressure of the trapped air is given by $P = 29\frac{2}{16} + h$, and the volume is directly proportional to l. If *(1.6)* is valid, then the product Pl should be constant. For the first data point,

$$Pl = (29\tfrac{2}{16} + 2\tfrac{13}{16})(44) = 1410$$

Likewise, the other products of Pl are all equal to 1410. Under these conditions, *(1.6)* is valid.

1.18 What pressure is required to compress an ideal gas from 10.0 ft^3 and 1.00 atm to 2.00 ft^3 under isothermal conditions?

▮ In terms of two different pressures and volumes, *(1.6)* can be written as

$$P_1V_1 = P_2V_2 \tag{1.7}$$

Solving *(1.7)* for P_2 and substituting the data gives

$$P_2 = (1.00\ \mathrm{atm})\frac{10.0\ \mathrm{ft}^3}{2.00\ \mathrm{ft}^3} = 5.00\ \mathrm{atm}$$

The pressure on the gas sample must be increased to 5.00 atm (= 5.07 bar).

1.19 A commercial gas cylinder contains 75 L of helium at 15 bar (gauge pressure). Assuming ideal gas behavior for the isothermal expansion, how many 3.0-L balloons at a pressure of 1.1 bar can be filled by the gas in this cylinder?

▮ Assuming that the atmospheric pressure is 1 bar, the initial and final pressures of the helium are

$$P_1 = 15\ \mathrm{bar} + 1\ \mathrm{bar} = 16\ \mathrm{bar} \qquad \text{and} \qquad P_2 = 1.1\ \mathrm{bar}$$

The final volume of the helium is given by *(1.7)* as

$$V_2 = (75\ \mathrm{L})\frac{16\ \mathrm{bar}}{1.1\ \mathrm{bar}} = 1100\ \mathrm{L}$$

Subtracting the 75 L that will remain in the cylinder, the number of balloons is

$$\frac{1100\ \mathrm{L} - 75\ \mathrm{L}}{3.0\ \mathrm{L}\cdot\mathrm{balloon}^{-1}} = 340\ \mathrm{balloons}$$

1.20 A diver at a depth of 45 m exhales a bubble of air that is 1.0 cm in radius. Assuming ideal gas behavior, what will be the radius of this bubble as it breaks the surface of the water?

▮ The volume of the bubble at 45 m is $V_1 = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(1.0\ \mathrm{cm})^3 = 4.2\ \mathrm{cm}^3$. The original pressure on the bubble is the sum of the pressure exerted by the water, given by *(1.4)*, plus the atmospheric pressure:

$$\begin{aligned} P_1 &= \rho g h + 1.0\ \mathrm{bar} \\ &= (1.00\ \mathrm{g}\cdot\mathrm{cm}^{-3})\frac{10^{-3}\ \mathrm{kg}}{1\ \mathrm{g}}\left(\frac{10^2\ \mathrm{cm}}{1\ \mathrm{m}}\right)^3(9.81\ \mathrm{m}\cdot\mathrm{s}^{-2})(45\ \mathrm{m})\frac{1\ \mathrm{N}}{1\ \mathrm{kg}\cdot\mathrm{m}\cdot\mathrm{s}^{-2}}\left(\frac{1\ \mathrm{bar}}{101\,325\ \mathrm{N}\cdot\mathrm{m}^{-2}}\right) + 1.0\ \mathrm{bar} \\ &= 5.4\ \mathrm{bar} \end{aligned}$$

The volume of the bubble at $P_2 = 1.0\ \mathrm{bar}$ is given by *(1.7)* as

$$V_2 = (4.2\ \mathrm{cm}^3)\frac{5.4\ \mathrm{bar}}{1.0\ \mathrm{bar}} = 23\ \mathrm{cm}^3$$

which corresponds to

$$r = \left(\frac{3V}{4\pi}\right)^{1/3} = \left(\frac{3(23\ \mathrm{cm}^3)}{4\pi}\right)^{1/3} = 1.8\ \mathrm{cm}$$

1.21 A 1.103-L flask containing nitrogen at a pressure of 710.6 torr is connected to an evacuated flask of unknown volume. The nitrogen, which acts ideally, is allowed to expand into the combined system of both flasks isothermally. If the final pressure of the nitrogen is 583.1 torr, determine the volume of the evacuated flask.

▮ The initial and final volumes of the nitrogen are

$$V_1 = 1.103\ \mathrm{L} \qquad \text{and} \qquad V_2 = 1.103\ \mathrm{L} + V$$

where V is the volume of the evacuated flask. Substituting the data into *(1.7)* and solving for V gives

$$(710.6\ \mathrm{torr})(1.103\ \mathrm{L}) = (583.1\ \mathrm{torr})(1.103\ \mathrm{L} + V)$$

$$V = 0.241\ \mathrm{L}$$

1.22 A McLeod gauge (a device for measuring low pressures in vacuum systems) is shown in Fig. 1-3. As the mercury is drawn into the gauge, a fixed volume of gas (V_{bulb}) is trapped in the bulb and compressed into a capillary tube at the top of the bulb. The two distances h_1 and h_2 are measured, and the pressure is given by *(1.7)* as

$$P/(\mathrm{torr}) = \frac{[(h_1 + h_2)/(\mathrm{mmHg})]\,V_{\mathrm{gas}}}{V_{\mathrm{bulb}}}$$

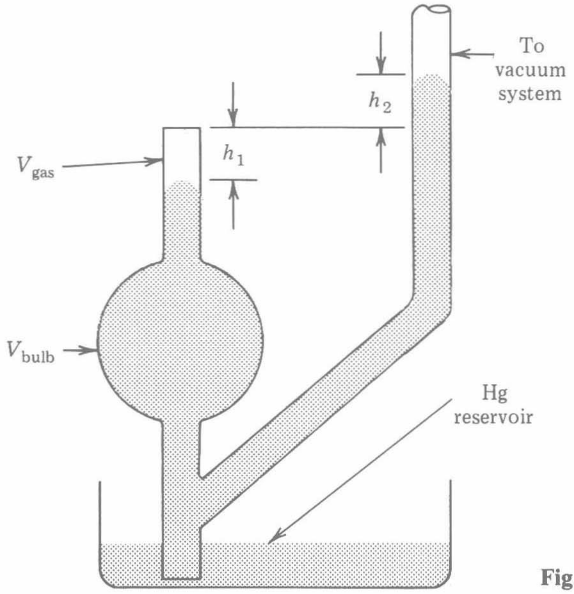

Fig. 1-3

Determine the pressure in a vacuum system given that $h_1 = 35$ mm, $h_2 = 82$ mm, $V_{bulb} = 100.3\ \text{cm}^3$, and the radius of the capillary tube is 0.25 mm.

■ The volume of the compressed gas is

$$V_{gas} = 4\pi r^2 h_1 = 4\pi(0.25\ \text{mm})^2(35\ \text{mm})\left(\frac{10^{-1}\ \text{cm}}{1\ \text{mm}}\right)^3 = 2.7 \times 10^{-2}\ \text{cm}^3$$

The pressure is

$$P/(\text{torr}) = \frac{(35 + 82)(2.7 \times 10^{-2}\ \text{cm}^3)}{100.3\ \text{cm}^3} = 3.1 \times 10^{-2}$$

which is equivalent to

$$P = (3.1 \times 10^{-2}\ \text{torr})\frac{1\ \text{atm}}{760\ \text{torr}}\left(\frac{101\ 325\ \text{Pa}}{1\ \text{atm}}\right) = 4.1\ \text{Pa}$$

1.23 Derive an expression for $(\partial V/\partial P)_{T,n}$ for an ideal gas. Evaluate the *isothermal compressibility*

$$\kappa = \left(-\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_{T,n} \tag{1.8}$$

for an ideal gas at 1.00 bar.

■ Solving *(1.6)* for V and taking the derivative with respect to P gives

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} = \left(\frac{\partial(k/P)}{\partial P}\right)_{T,n} = -\frac{k}{P^2} = -\frac{PV}{P^2} = -\frac{V}{P}$$

The isothermal compressibility is given by *(1.8)* as

$$\kappa = \left(-\frac{1}{V}\right)\left(-\frac{V}{P}\right) = \frac{1}{P} = \frac{1}{1.00\ \text{bar}} = 1.00\ \text{bar}^{-1}$$

1.24 Identify which of the following plots for a fixed amount of an ideal gas at constant pressure will be linear: **(*a*)** V vs. T, **(*b*)** V vs. $1/T$, **(*c*)** V/T vs. T, and **(*d*)** VT vs. V. Determine the slope of the straight line in each linear plot.

■ The volume-temperature behavior for a fixed amount of an ideal gas under isobaric conditions is given by *Charles's law* as

$$V = kT \tag{1.9}$$

where k is a constant. The linear forms of *(1.9)* are **(*a*)** $V = kT$ with the slope equal to k and **(*c*)** $V/T = k$ with the slope equal to 0.

1.25 A rubber balloon was filled with helium at 25 °C and placed in a beaker of liquid nitrogen at −196 °C. The volume of the cold helium was 15 cm^3. Assuming ideal gas behavior and isobaric conditions, what was the volume of the helium at 25 °C?

▌ In terms of two different volumes and temperatures, *(1.9)* can be written as

$$V_2/T_2 = V_1/T_1 \tag{1.10}$$

Solving *(1.10)* for V_2 and substituting the data gives

$$V_2 = (15\ \text{cm}^3)[(298\ \text{K})/(77\ \text{K})] = 58\ \text{cm}^3$$

1.26 To what temperature must an ideal gas be heated under isobaric conditions to increase the volume from 100 cm^3 at 25 °C to 1.00 dm^3?

▌ Solving *(1.10)* for T_2 and substituting the data gives

$$T_2 = (298\ \text{K})\frac{(1.00\ \text{dm}^3)[(10\ \text{cm})/(1\ \text{dm})]^3}{100\ \text{cm}^3} = 2980\ \text{K}$$

1.27 The volume of 1.00 mol of an ideal gas at 1.00 bar and 0 °C decreased to 21.1 L when placed in a methanol–ice bath. What was the temperature of the bath?

▌ For 1.00 mol of an ideal gas at 1.00 bar, *(1.9)* can be written as

$$V = V_0\{1 + \alpha[T/(°\text{C})]\}$$

where $V_0 = 22.7\ \text{L}$ and $\alpha = 3.66 \times 10^{-3}$. Solving for temperature and substituting the data gives

$$T/(°\text{C}) = \frac{V/V_0 - 1}{\alpha} = \frac{(21.1\ \text{L})/(22.7\ \text{L}) - 1}{3.66 \times 10^{-3}} = -19$$

The temperature of the bath was −19 °C.

1.28 Derive an expression for $(\partial V/\partial T)_{P,n}$ for an ideal gas. Evaluate the *cubic expansion coefficient*

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{1.11}$$

for an ideal gas at 0 °C.

▌ Solving *(1.9)* for V and taking the derivative with respect to T gives

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \left(\frac{\partial(kT)}{\partial T}\right)_{P,n} = k = \frac{V}{T}$$

The cubic expansion coefficient is

$$\alpha = \frac{1}{V}\left(\frac{V}{T}\right) = \frac{1}{T} = \frac{1}{273\ \text{K}} = 3.66 \times 10^{-3}\ \text{K}^{-1}$$

1.29 For a fixed amount of an ideal gas under constant-volume conditions, the pressure–temperature behavior is given by *Amonton's law* as

$$P = kT \tag{1.12}$$

where k is a constant. Evaluate k in terms of the isothermal compressibility, see *(1.8)*, and the cubic expansion coefficient, see *(1.11)*.

▌ Taking the derivative of P with respect to T gives

$$\left(\frac{\partial P}{\partial T}\right)_V = k$$

Expressing the same derivative in terms of $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ (see Table 6-3) gives

$$k = \left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{(1/V)(\partial V/\partial T)_P}{-(1/V)(\partial V/\partial P)_T} = \frac{\alpha}{\kappa}$$

1.30 The pressure in an ideal gas thermometer increased from 589 torr to 785 torr when the thermometer bulb was transferred from an ice-water bath at 0 °C to a beaker of boiling water. Assuming that the volume of the thermometer bulb did not change, what was the temperature of the boiling water?

▌ In terms of two different pressures and temperatures, *(1.12)* can be written as

$$P_2/T_2 = P_1/T_1 \tag{1.13}$$

Solving *(1.13)* for T_2 and substituting the data gives

$$T_2 = (273\ \text{K})\frac{785\ \text{torr}}{589\ \text{torr}} = 364\ \text{K} = 91\ °\text{C}$$

1.31 The pressure of air in an automobile tire at 15 °C was 32 psig. After the tire warmed to 35 °C from driving, what was the air pressure? Did it exceed the recommended maximum pressure of 34 psig?

▌ Assuming an atmospheric pressure of 15 psi, the original pressure was $P_1 = 32\ \text{psi} + 15\ \text{psi} = 47\ \text{psi}$. Solving *(1.13)* for P_2 and substituting the data gives

$$P_2 = (47\ \text{psi})\frac{308\ \text{K}}{288\ \text{K}} = 50\ \text{psi} = 35\ \text{psig}$$

which slightly exceeds the recommended maximum pressure.

1.32 According to *Gay-Lussac's law of combining volumes*, 2 L of hydrogen gas will react with 1 L of oxygen gas (measured at the same temperature and pressure) to produce steam. What volume of steam will be formed?

▌ The relationship between the volume and the amount of substance (commonly known as the "number of moles," n) for an ideal gas under constant pressure and temperature conditions is given by *Avogadro's hypothesis*

$$V = kn \tag{1.14}$$

where k is constant. From the balanced chemical equation describing the reaction,

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

we can easily see that $k = 1$ in this case, so 2 L or 2 mol of hydrogen gas will react with 1 L or 1 mol of oxygen gas to produce 2 L or 2 mol of steam.

1.33 A toy balloon originally held 1.00 g of helium gas and had a radius of 10.0 cm. During the night, 0.25 g of the gas effused from the balloon. Assuming ideal gas behavior under these constant pressure and temperature conditions, what was the radius of the balloon the next morning?

▌ In terms of two different volumes and amounts of substance, *(1.14)* can be written as

$$V_1/n_1 = V_2/n_2 \tag{1.15}$$

Solving *(1.15)* for V_2 and substituting the data gives

$$V_2 = \tfrac{4}{3}\pi(10.0\ \text{cm})^3\frac{(0.75\ \text{g})/(4.00\ \text{g}\cdot\text{mol}^{-1})}{(1.00\ \text{g})/(4.00\ \text{g}\cdot\text{mol}^{-1})} = 3100\ \text{cm}^3$$

which corresponds to a radius of

$$r = (3V/4\pi)^{1/3} = [3(3100\ \text{cm}^3)/4\pi]^{1/3} = 9.0\ \text{cm}$$

1.34 Derive an expression for $(\partial V/\partial n)_{T,P}$ for an ideal gas. What will be the volume change corresponding to an increase of 0.01 mol at 25 °C and 1.00 bar? The molar volume of an ideal gas under these conditions is 24.8 L · mol^{-1}.

▌ Taking the derivative of *(1.14)* with respect to n gives

$$\left(\frac{\partial V}{\partial n}\right)_{T,P} = \left(\frac{\partial kn}{\partial n}\right)_{T,P} = k = \frac{V}{n}$$

The value of k under these conditions is

$$k = \frac{V}{n} = \frac{24.8\ \text{L}}{1.00\ \text{mol}} = 24.8\ \text{L}\cdot\text{mol}^{-1}$$

The volume change is found by integrating the expression for $(\partial V/\partial n)_{T,P}$:

$$\int_{V_1}^{V_2} dV = \int_{n_1}^{n_2} k\,dn$$

$$\Delta V = k\,\Delta n = (24.8\ \text{L}\cdot\text{mol}^{-1})(0.01\ \text{mol}) = 0.2\ \text{L}$$

1.35 The pressure of a fixed amount of an ideal gas is 0.750 bar. What will be the pressure after the volume of the gas is tripled and the absolute temperature is doubled?

▮ Combining *(1.6)* and *(1.9)* gives the *combined gas law*

$$PV/T = k \tag{1.16}$$

where k is a constant. For two different sets of conditions, *(1.16)* can be written as

$$P_1V_1/T_1 = P_2V_2/T_2 \tag{1.17}$$

Solving *(1.17)* for P_2 and substituting the data gives

$$P_2 = (0.750\ \text{bar})\frac{V_1}{3V_1}\left(\frac{2T_1}{T_1}\right) = 0.500\ \text{bar}$$

1.36 An ideal gas sample had a volume of 1.00 L at sea-level conditions of 1.01 bar and 18 °C. As the gas enters the thermosphere at 500 km, the volume increases to 3.5×10^{11} L at a pressure of 1.5×10^{-11} bar. What is the temperature of the gas at this altitude?

▮ The final temperature of the gas is given by *(1.17)* as

$$T_2 = (291\ \text{K})\frac{1.5 \times 10^{-11}\ \text{bar}}{1.01\ \text{bar}}\left(\frac{3.5 \times 10^{11}\ \text{L}}{1.00\ \text{L}}\right) = 1500\ \text{K}$$

1.37 The volume of one mole of an ideal gas at STP (273.15 K and exactly 1 atm) is 22.4138 L. The "standard ambient temperature and pressure" (SATP) is defined as 298.15 K and exactly 1 bar. What is the molar volume under these new standard conditions?

▮ Solving *(1.17)* for V_2 and substituting the data gives

$$V_2 = (22.4138\ \text{L})\frac{(1\ \text{atm})[(1.013\,25\ \text{bar})/(1\ \text{atm})]}{1\ \text{bar}}\left(\frac{298.15\ \text{K}}{273.15\ \text{K}}\right) = 24.7894\ \text{L}$$

1.38 What is the mass of air in a 250-mL Erlenmeyer flask (actual volume is 267 mL) at a typical laboratory pressure of 715 torr and a temperature of 21 °C? Assume air to be an ideal gas having an average molar mass of 29.0 $\text{g} \cdot \text{mol}^{-1}$.

▮ The pressure–volume–temperature–amount of substance relationship for an ideal gas is given by the *ideal gas law*

$$PV = nRT \tag{1.18}$$

where R is given in Table 1-2. The amount of air is

$$n = \frac{PV}{RT} = \frac{(715\ \text{torr})[(1\ \text{atm})/(760\ \text{torr})](267\ \text{mL})[(10^{-3}\ \text{L})/(1\ \text{mL})]}{(0.0821\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(294\ \text{K})} = 0.0104\ \text{mol}$$

which corresponds to

$$m = nM = (0.0104\ \text{mol})(29.0\ \text{g}\cdot\text{mol}^{-1}) = 0.302\ \text{g}$$

Table 1-2

$8.314\,41\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$8.314\,41\ \text{m}^3\cdot\text{Pa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$0.083\,144\,1\ \text{L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$0.082\,056\,8\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

1.39 What volume of hydrogen will be produced at 0.963 bar and 28 °C from the reaction of 6.0 g of zinc with excess 6 M hydrochloric acid? Assume that hydrogen is an ideal gas under these conditions.

▮ The amount of zinc reacting is

$$n = \frac{m}{M} = \frac{6.0\ \text{g Zn}}{65.39\ \text{g} \cdot \text{mol}^{-1}} = 0.092\ \text{mol Zn}$$

The chemical equation $\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$ shows that the amount of hydrogen produced is

$$(0.092\ \text{mol Zn})\frac{1\ \text{mol H}_2}{1\ \text{mol Zn}} = 0.092\ \text{mol H}_2$$

Solving *(1.18)* for V and substituting the data gives

$$V = \frac{(0.092\ \text{mol})(0.083\,14\ \text{L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(301\ \text{K})}{0.963\ \text{bar}} = 2.4\ \text{L}$$

1.40 The relative humidity in a room is 65%. Assuming ideal gas behavior, what mass of water vapor is in the air at 25 °C if the room measures 4 m × 4 m × 3 m? The vapor pressure of liquid water is 23.8 torr at 25 °C.

▮ The *relative humidity* is the actual vapor pressure of water vapor in the air divided by the equilibrium vapor pressure of water at that temperature and is usually expressed as a percentage. The pressure of the water vapor in this case is

$$P = (0.65)(23.8\ \text{torr}) = 15.5\ \text{torr}$$

which upon substitution into *(1.18)* gives the amount of water as

$$\begin{aligned} n &= \frac{(15.5\ \text{torr})[(1\ \text{atm})/(760\ \text{torr})][(101\,325\ \text{Pa})/(1\ \text{atm})][(4\ \text{m})(4\ \text{m})(3\ \text{m})]}{(8.314\ \text{m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298\ \text{K})} \\ &= 40\ \text{mol} \end{aligned}$$

which corresponds to

$$m = nM = (40\ \text{mol})(18\ \text{g} \cdot \text{mol}^{-1}) = 700\ \text{g}$$

1.41 The vapor pressure of liquid water is 23.8 torr at 25 °C. By what factor does the molar volume of water increase as it vaporizes to form an ideal gas under these conditions? The density of liquid water is $0.997\ \text{g} \cdot \text{cm}^{-3}$ at 25 °C.

▮ Substituting *(1.18)* for the volume of the vapor into the expression for the ratio of the volumes gives

$$\begin{aligned} \frac{V(\text{gas})}{V(\text{liquid})} &= \frac{RT/P}{M/\rho} = \frac{RT\rho}{MP} \\ &= \frac{(0.083\,14\ \text{L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298\ \text{K})(0.997\ \text{g} \cdot \text{cm}^{-3})[(10^3\ \text{cm}^3)/(1\ \text{L})]}{(18.0\ \text{g} \cdot \text{mol}^{-1})(23.8\ \text{torr})[(1\ \text{atm})/(760\ \text{torr})][(1.013\,25\ \text{bar})/(1\ \text{atm})]} \\ &= 4.32 \times 10^4 \end{aligned}$$

1.42 What is the value of the gas constant expressed in units of $\text{L} \cdot \text{torr} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$?

▮ Using appropriate conversion factors gives

$$\begin{aligned} R &= (8.314\,41\ \text{m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})\frac{10^3\ \text{L}}{1\ \text{m}^3}\left(\frac{1\ \text{atm}}{101\,325\ \text{Pa}}\right)\left(\frac{760\ \text{torr}}{1\ \text{atm}}\right) \\ &= 62.3632\ \text{L} \cdot \text{torr} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

1.43 Prepare a plot of PV/T against P to determine R from the following data for CO_2 at 0 °C:

$P/(\text{atm})$	0.500	0.100	0.010
$V/(\text{L} \cdot \text{mol}^{-1})$	44.672	223.980	2241.204

▮ The respective values of $(PV/T)/(\text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$ are 0.081 771, 0.081 998, and 0.082 050. The intercept of the plot shown in Fig. 1-4 gives $R = 0.082\,055\ \text{L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.